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Morphological control of silicate mesostructures using flat and grooved substrates

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Morphologies of silicate hexagonal mesostructures deposited on substrates were investigated using a surfactant-templated synthesis. Truncated cone-like morphologies were produced on flat substrates with a smooth surface although silicate particles with complex shapes including gyroids and spheroids were precipitated in precursor solutions. Multilayered tower-like structures were found to be constructed on the truncated cones. Oriented silicate rods were observed on a substrate with microgrooves. These results indicate that the morphology of deposited silicate mesostructures is influenced by the surface state of substrates.
Key words: mesophase, silica, templating, surfactant, morphology

1. INTRODUCTION

Mesoscopically ordered silicate materials have been synthesized by the organization of surfactant molecules and silica precursor species [1,2]. The formation of various kinds of mesophases of the silica composites similar to liquid crystal array was reported, such as hexagonal, cubic and lamellar [2]. The morphological study revealed that the hexagonally ordered silicate shows noncrystallografical shapes including curved wormlike and tubuler particles [3]. Since oriented mesophase will be useful for many applications, such as selective membranes, the control of the morphology of silicate mesostructures is extremely important. Oriented mesostructured silica films were reported to be formed at the mica-water, graphite-water and air-water interfaces [4-6]. Microscopic patterning of oriented mesostructures was successfully prepared by infiltrating a reaction fluid in to microcapillaries [7]. However, these techniques suffer from several limitations because only few kinds of substrates or arrangements are applicable for the controlled synthesis. Although the control of the non-crystallographic morphologies is necessary for understanding of self-assembly of ceramics-surfactant complex and its applications as a novel microfabrication technique, it has not been exactly achieved and the underlying mechanism is still unknown.

Here, we demonstrate the morphological control of silicate mesostructures using several kinds of substrates. Flat and grooved surfaces were found to be useful for controlling the morphology and the orientation of the silicate mesostructures deposited.

2. EXPERIMENTAL PROCEDURE

Mesostructured silicate was prepared under acidic conditions containing tetraethoxysilane (TEOS) and cetyltrimethylammonium chloride (CTAC). Typical molecular ratios for the precursor solutions are 1 TEOS: 1.3 CTAC: 2.4 HCl : 280 water. The mixed solutions were stirred at room temperature for 1h. Polished silicon wafer and grooved silicone plates were immersed in the mixed mixed solutions and then kept at room temperature. The surface for the deposition was covered or arranged downward to prevent accumulation of precipitates. Silicate deposited on the substrates was characterized by XRD (Rikagu RAD-C), infrared absorption (Bio Rad FTS-165), optical microscopy and SEM observation (Hitachi S-2150).

3. RESULTS AND DISCUSSION

As shown in Fig 1, particles precipitated in the mixed solutions had complex shapes including gyroids and spheroids. The XRD pattern (Fig. 2) and the FTIR absorption spectra revealed that the precipitates consisted of surfactant-silicate composite having a hexagonal unit cell with a~ 4.4 nm. Well-defined faceting of the precipitates showing hexagonal basal faces is ascribed to hexagonally aligned surfactant-silicate micelles. As shown in Fig. 3, truncated cone-like morphologies were found to be formed on a flat substrate with a smooth surface. The faceting of the body and the XRD pattern indicate that the cones are also based on the hexagonal planes. Since the top face of the truncated body was parallel to the surface,

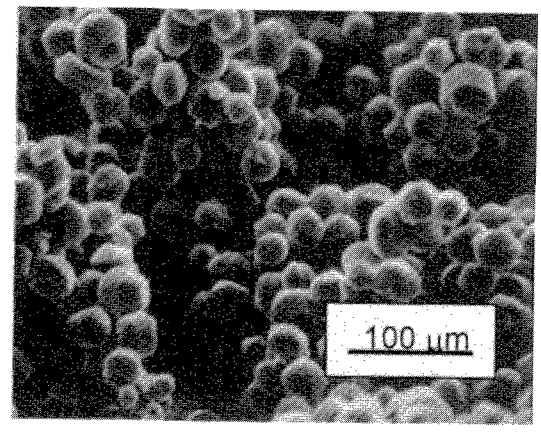

FIg. 1 SEM image of the precipitates.

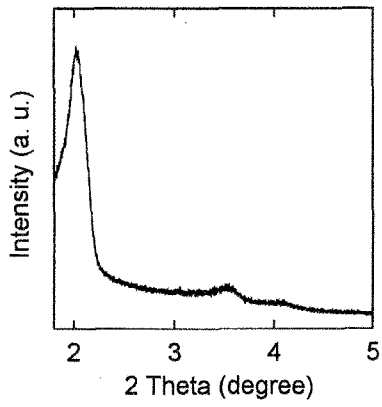

Fig. 2 XRD pattern of the precipitates.

the deposition of the surfactant-silicate micelles was regulated by the surface plane. Thus, the hexagonally ordered silicate is suggested to be formed through heterogeneous nucleation on the surface. Small truncated cones were found to grew from the basal cones with increasing the deposition time. While the orientation of the small cones was usually random, multilayered tower-like morphologies were occasionally observed (Fig. 4). The direction of the growth of the towers was exactly perpendicular to the surface. Since the faceting of the towers exhibits hexagonal basal faces and is parallel to each other, the towers are suggested to be constructed on a plane surface of the basal truncated cones without the irregularly grown small cones. The hexagonal mesophase was proposed to be transformed from a

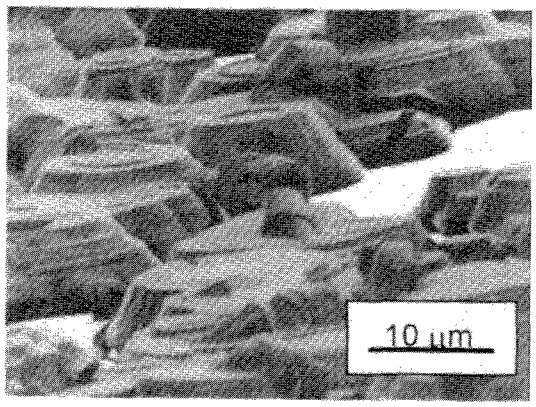

Fig. 3 SEM image of truncated cones deposited on a flat silica surface.

lamellar of the surfactant-inorganic systems [2,8]. In this case, however, the hexagonal array is deduced to be directly assembled by the basal surface of the substrate.

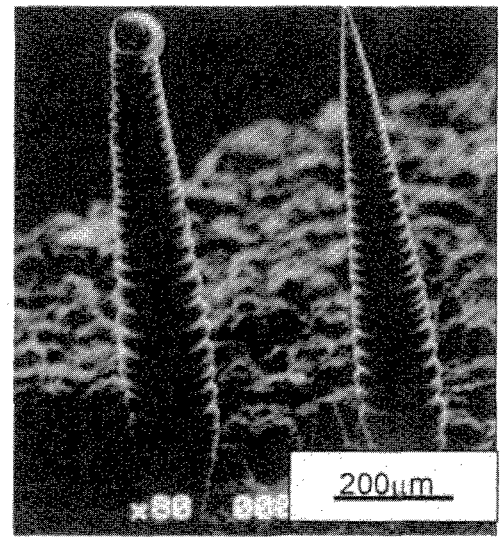

Fig. 4 SEM image of tower-like morphology on a flat silica surface.

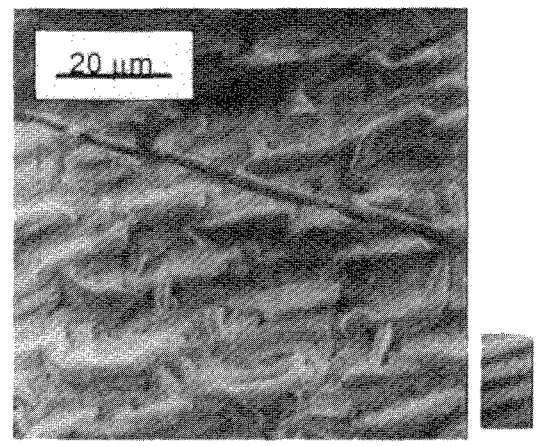

Fig. 5 SEM image of oriented rods on a grooved surface. The original grooves are shown in the side image. The width and the depth of the grooves were 2 μm.

Rod-like deposition showing hexagonal basal faces was observed on a microgrooved substrate. The XRD pattern indicated that the deposition also consisted of a hexagonal unit cell. As shown in Fig. 5, the hexagonal rods are found to be aligned along with the microgrooves on the substrate. The orientation of the growth of the rods was regulated by the wall of the grooves. Thus, the hexagonal mesophase is suggested to be oriented along with the grooves. Oriented mesostructured silica films were reported to be formed on a freshly cleaved mica surface and graphite surfaces [4,6]. In these cases, the nanoscaled crystal lattice of the surfaces controls the orientation of the deposition. On the other hand, our results indicate that microscaled structures also regulates the alignment of the

mesophases.

4. CONCLUSIONS

We investigated the morphologies of hexagonally ordered surfactant-silicate mesostructures deposited on various kinds of substrates. Multilayered tower-like structures and oriented hexagonal rods were prepared by controlling the deposition condition and the surface state of the substrates. We expect that these results are useful for the synthesis of macroscopically controlled surfactant-silicate mesostructures.

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